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**Reactive Ion Etching  
for Randomly Distributed Texturing of  
Multicrystalline Silicon Solar Cells**

**Annual Report**

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## EXECUTIVE SUMMARY

We have applied reactive ion etching techniques that produce random texturing to a wide range of multicrystalline silicon solar cells with surface areas in the 4-130 cm<sup>2</sup> range. Using these texturing techniques, broadband spectral reflection < 1 % for wavelengths < 1 μm has been achieved. Solar cells fabricated using RIE-texturing techniques failed to translate these substantial gains in optical absorption into higher efficiencies due in part to plasma-induced surface damage and contamination. By employing inexpensive, wet-chemical post-RIE damage removal treatments, surface damage and contamination were eliminated without significant reflection increases. Random, RIE-textured solar cells with DRE treatments fabricated at BP Solar, Siemens, Australian National University, Sandia National Laboratories, and Georgia Institute of Technology exhibited significant performance gains. The performance gains in efficiency and short circuit current were largest at ~ 8 % and 13 % respectively for the smallest area (~ 4 cm<sup>2</sup>) and lowest at ~ 1.5 % and 1 % respectively for the largest area (~ 130 cm<sup>2</sup>) solar cells. This area-related performance deficiency is attributed to several factors including texture non-uniformity, lack of optimum emitter formation, and the use of non-passivating TiO<sub>2</sub> anti-reflection films. Emitter passivation has been identified as an important parameter, since despite appropriate DRE treatments, the RIE-textured solar cells processed at several other PV manufacturers performed poorly. By improving texture uniformity to the wafer edges, optimizing wet-chemical DRE treatment coupled with high-quality emitter formation, we expect large area cell performance gains in the 10-20 % range.

## **TABLE OF CONTENTS**

1. Introduction	4
2. Solar Cells Processed at BP Solar	6
3. Solar Cells Processed at Australian National University	9
4. Solar Cells Processed at Siemens	10
5. Solar Cells Processed at Sandia National Laboratories	11
6. Solar Cells Processed at Georgia Institute of Technology	13
7. Summary and Future Work	15
8. References	17
9. Acknowledgements	17

## 1. INTRODUCTION

The quality of low-cost multicrystalline silicon (mc-Si) has improved to the point that it forms approximately 50 % of the worldwide photovoltaic (PV) power production. The performance of commercial mc-Si solar cells still lags behind c-Si due in part to the inability to texture it effectively and inexpensively. Surface texturing of mc-Si has been an active field of research. Several techniques including anodic etching [1], wet acidic etching [2], lithographic patterning [3], and mechanical texturing [4] have been investigated with varying degrees of success. To date, a cost-effective technique has not emerged.

In recent years, maskless reactive ion etching texturing techniques have received significant attention [5-7]. Reactive ion etching (RIE) texturing techniques to produce randomly distributed texture take advantage of the extensive infrastructure developed for Si microelectronics, and as such can lead to significant savings in tool development efforts for the PV manufacturers. As worldwide PV demands increase, the use of thinner ( $\leq 100\ \mu\text{m}$ ) mc-Si substrates is expected to increase substantially. In this context, RIE texturing techniques are critically important not only for their proven ability to reduce broadband spectral reflection ( $< 1\%$  for  $\lambda < 1\ \mu\text{m}$ ), but also their ability to enhance oblique coupling of incident light into the semiconductor substrate. For a weakly absorptive medium such as Si in near IR spectral range, statistical analysis by Yablonovitch has shown that optical absorption with a lambertian surface can be enhanced by  $\sim 4n^2$  relative to a planar surface, where  $n$  is the refractive index [8]. In order to reach this statistical limit, typical texture dimensions have to be comparable, or larger than the optical wavelengths of interest [9]. If texture dimensions are smaller than the optical wavelengths, scattering is not effective due to the inability to resolve the texture. We have described this interdependence between the texture dimension and optical light interaction in terms of enhanced coupling into obliquely propagating transmitted diffraction order modes [10]. Creation of electron-hole pairs close to the front surface increases the probability of their separation by the junction field due to reduced bulk recombination losses.

Gratings, Incorporated (GI) in collaboration with Sandia National Laboratories (SNL) has developed large area ( $\sim 187\ \text{cm}^2$ ), maskless random RIE texturing techniques [11-13]. These techniques employ a metal-catalyst approach to tune microstructure profile and dimension for improving the solar cell performance. Figure 1 shows three types of profiles achieved using these methods. Comparison of feature dimensions shows that Cr-assisted supports smallest  $\sim 0.3\ \mu\text{m}$  average separation, Al and conditioned texture average separations are typically an order of magnitude larger with columnar and triangular profiles. The hemispherical spectral reflectance measurements from the three RIE-textured surfaces in Figure 1 are shown in Figure 2. It is seen that lowest reflectance is observed from conditioned texture, highest from the Al-assisted. In general, reflection increases as feature dimensions are increased.

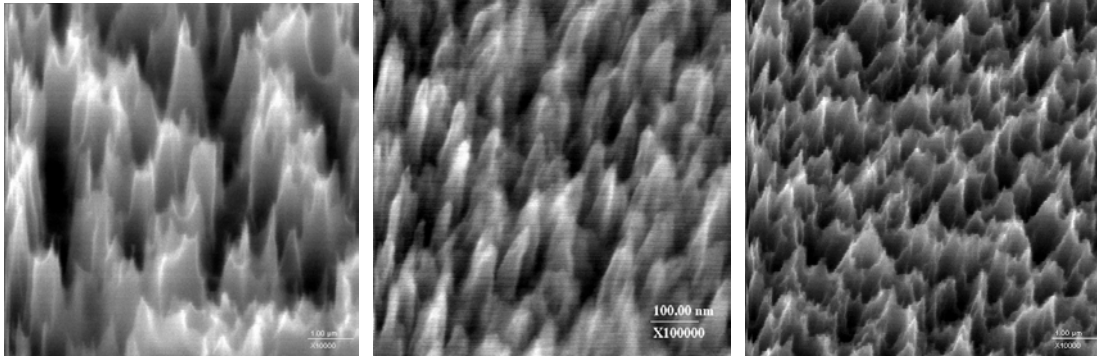


Figure 1. SEM pictures of three random RIE texture profiles, Al-assisted (left), Cr-assisted (center), and conditioned (right), SEM length scales are 1- $\mu\text{m}$  for Al, the conditioned, and 0.1- $\mu\text{m}$  for Cr.

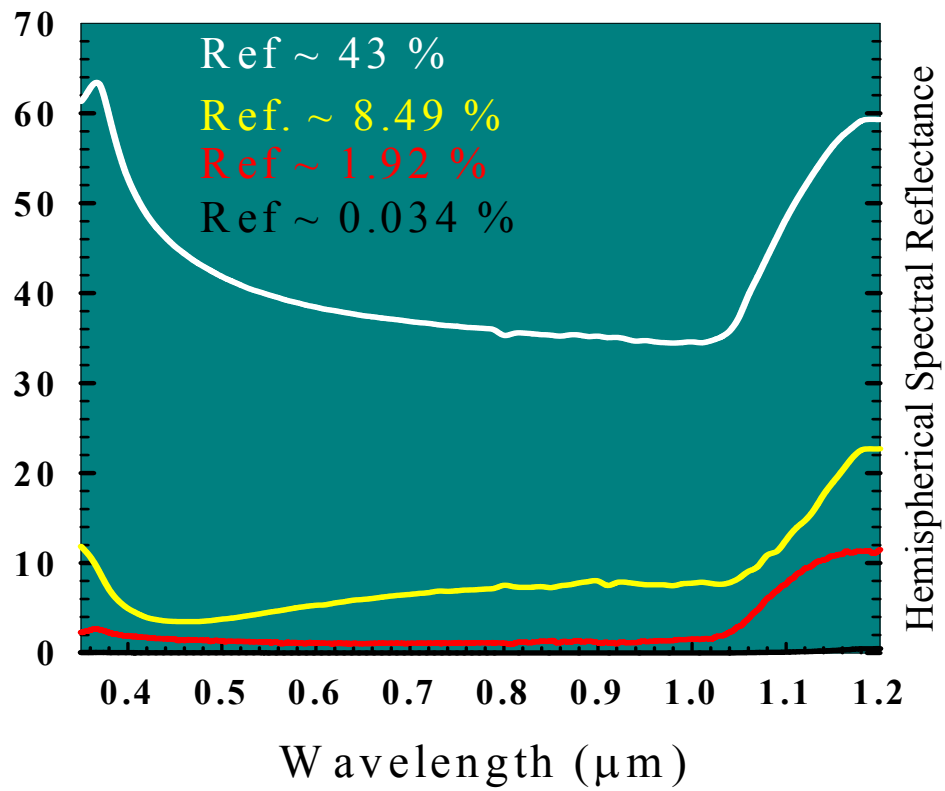


Figure 2. Absolute hemispherical spectral reflectance measurements from several textured surfaces, no anti-reflection films were used.

Initial solar cell fabrication on RIE-textured single crystalline surfaces revealed that the benefits of lower reflection were not realized in improved solar cell performance due to several contributing factors including contamination, RIE-induced surface damage, and the lack of optimum emitter formation. By incorporating a complete RCA clean process followed by nitric acid wet-chemical damage removal treatment, solar cell performance comparable to wet-chemically etched c-Si cells was achieved [12-13]. Random, RIE-texturing techniques have been adapted to a wide range of multicrystalline Si wafers from several commercial sources including AstroPower, ASE Americas, Ebara, Inc., BP Solar, and Siemens/Shell. Several performance-reducing issues have been identified including RIE-induced surface damage and the formation of an optimum emitter. Formation of an optimum emitter over textured surface may be one of the critical factors. For instance, the performance of RIE-textured solar cells processed at AstroPower, ASE, and Ebara has been poor, whereas, on similar surfaces, solar cells processed at BP Solar and Siemens have demonstrated considerable performance gains.

The remainder of this report has been divided into sections 2-6 describing mc-Si solar cell performance in order of decreasing surface areas from  $\sim 130 \text{ cm}^2$  to  $\sim 4 \text{ cm}^2$ . Section 7 discusses results and the plans for further improvements, references are provided in section 8, and acknowledgments in section 9.

## 2. SOLAR CELLS PROCESSED AT BP SOLAR

In collaboration with SNL and GI, BP Solar has been evaluating random, RIE-texturing techniques aimed at cost-effective improvement of their large area ( $\sim 130 \text{ cm}^2$ ) mc-Si solar cells. As part of this collaborative research effort, RIE-textured surfaces were processed into solar cells under a wide range of processing parameters including:

- a) Evaluation of several textures to determine an optimum profile beneficial for solar cell performance,
- b) An assessment of RCA clean process in solar cell manufacturing environment, and
- c) The optimization of post-RIE, wet-chemical damage removal etches (DREs).

All the solar cells were fabricated on random, RIE-textured,  $\sim 130\text{-cm}^2$  area wafers and coated with anti-reflection  $\text{TiO}_2$  films using screen-printed contacts in a production line environment. For all the textured solar cells, sister control (planar) wafers were processed at the same time to account for material and process variations. For all the data plotted here, averages were taken from at least  $\sim 10$ -12 cells subjected to the same processing conditions. Figure 3 shows efficiency and short circuit current for three RIE-textured surfaces shown in Figure 1. We notice that the Cr-assisted textured surface performance is almost comparable to the planar, the other two textured surfaces perform poorly. It appears that the cell performance decreases as texture dimensions increase.

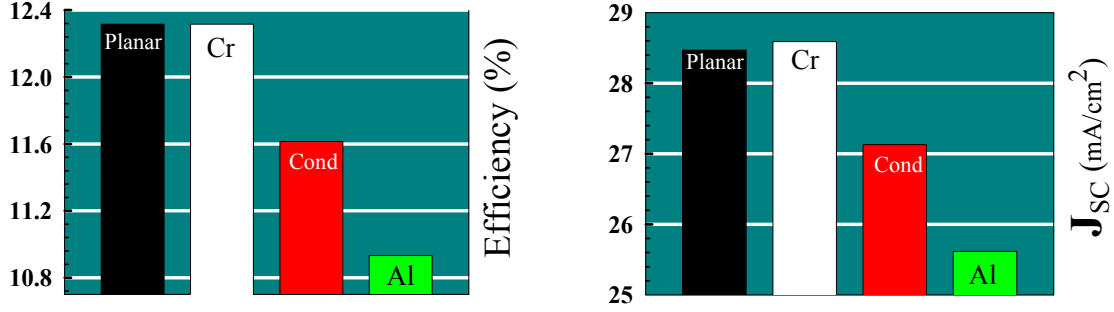


Figure 3. BP Solar cell efficiency (left) and short circuit current ( $J_{SC}$ , right) measurements for three RIE-texturing processes used, results from control cells are also plotted for comparison.

This lack of performance enhancement despite substantial reflection losses has been attributed to RIE-induced surface damage and contamination [12-14]. Complete RCA clean combined with nitric acid based DRE (#1) treatments have been investigated.

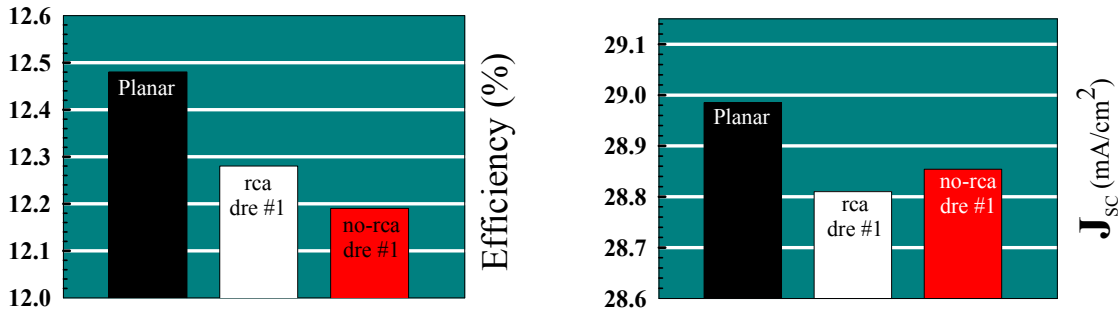


Figure 4. BP Solar cell efficiency (left) and  $J_{SC}$  (right) measurements for conditioned, RIE-texturing process with and without RCA clean, while keeping same DRE and texture processes, control cell data is also plotted for comparison.

Figure 4 shows the cell performance with and without RCA clean process. For these cells, same conditioned texture and the nitric DRE treatments were employed. The RCA comparison shows that there is little performance gain from its inclusion in cell fabrication. It is likely that the small performance gain arises from the non-uniformity in the nitric DRE process. This is an important result, since the RCA clean process increases solar cell fabrication costs. Figure 4 also shows that the DRE process has helped increase efficiency from  $\sim 11.6$  to  $12.3$ , and  $J_{SC}$  from  $27 \text{ mA/cm}^2$  to  $\sim 28.82 \text{ mA/cm}^2$ , although RIE-texture performance is still inferior to control cells. In order to remedy this, we have investigated several DRE processes. Best results have been achieved with an alkaline-based DRE (#2) process. Figure 5 shows that the RIE-textured surfaces subjected to DRE #2 outperform the planar controls. Further DRE optimization is expected to lead to significant performance gains. The critical role of post-RIE DRE treatments

is further clarified in Figure 6, which plots the absolute efficiency and efficiency ratios relative to the controls without the DRE and with the two DRE treatments. We notice that without the DRE treatment, RIE-textured solar cell efficiency relative to controls is reduced by  $\sim 5.7\%$ . By incorporating DRE # 1, the textured cell efficiency is only reduced by  $\sim 2.3\%$ , and finally with the DRE # 2, cell efficiency relative to controls is enhanced by  $\sim 0.88\%$ . Figure 7 shows similar results for  $J_{SC}$  measurements. The short circuit current relative to controls is reduced by  $\sim 4.78\%$  and  $\sim 0.45\%$  for solar cells without any DRE and with the DRE # 1; with DRE # 2, the current is enhanced by  $\sim 1.03\%$ . No RCA clean was performed prior to DRE treatments.

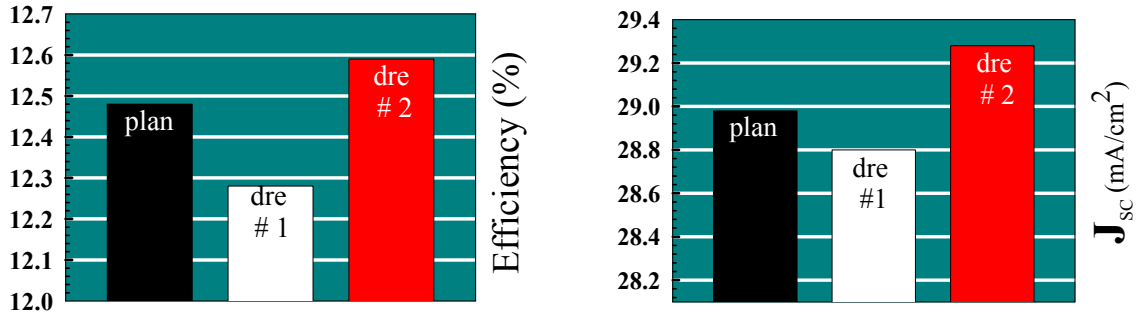


Figure 5. BP Solar cell efficiency (left) and  $J_{SC}$  (right) measurements for two DRE processes used, results from control cells processed at the same time are also plotted for comparison; no RCA clean was used.

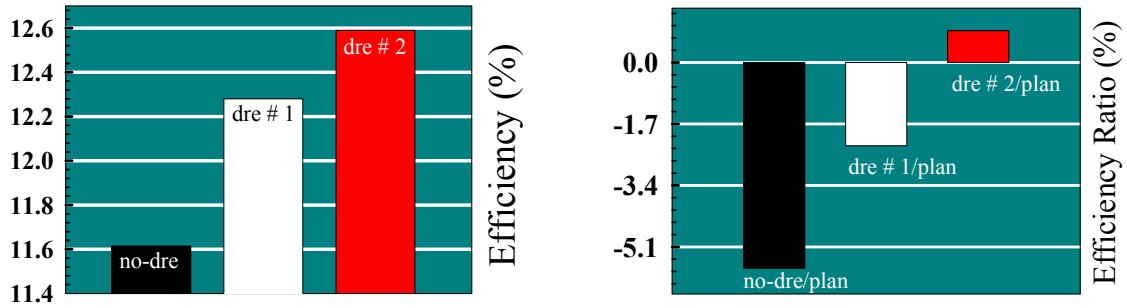


Figure 6. BP Solar cell efficiency (left) and efficiency ratios relative to the planar controls (right) for the conditioned texture process with out DRE and with two DRE treatments; no RCA clean was used.



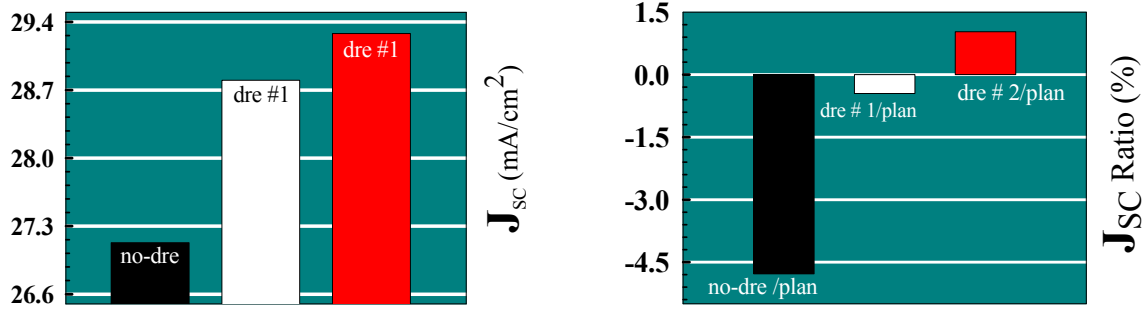


Figure 7. BP Solar cell  $J_{SC}$  (left) and  $J_{SC}$  ratios relative to the planar controls (right) for the conditioned texture process without DRE and with two DRE treatments, no RCA clean was used.

In summary, the RIE-textured cells outperforming controls have been demonstrated using a post-RIE, alkaline-based DRE treatment. The performance gains have been modest due to several contributing factors including lack of texture uniformity over entire surface, lack of optimization of the DRE treatment, lack of passivating anti-reflections films, and lack of optimum emitter formation on nano and microstructured surfaces. Research efforts aimed at the resolution of these issues in close collaboration with BP Solar are currently underway. The aim of these research efforts is to achieve significant ( $\sim 10\text{-}20\%$ ) performance gains from large ( $\geq 130\text{ cm}^2$ ) mc-Si solar cells.

### 3. SOLAR CELLS PROCESSED AT AUSTRALIAN NATIONAL UNIVERSITY

In collaboration with SNL, a number of  $130\text{-cm}^2$ -area bp solar wafers were RIE-textured, RCA cleaned, and subjected to nitric DRE. These wafers were subsequently processed into solar cells at the Australian National University (ANU). There were two major differences with the processing at BP Solar: a) Gaseous diffusion for emitter formation, and b) the use of nitride anti-reflection films formed by plasma enhanced chemical vapor deposition (PECVD) process instead of  $\text{TiO}_2$ . In order to isolate the influence of texture non-uniformity at the edges, efficiency and  $J_{SC}$  measurements were carried out from the as-fabricated  $130\text{-cm}^2$  cells and by dicing a uniform area of  $64\text{ cm}^2$  out of the wafer center. Figure 8 shows efficiency measurements from both cell areas. The efficiency improvement relative to control cells is  $\sim 1.5\%$  for  $130\text{-cm}^2$  area and  $\sim 1.8\%$  for  $64\text{-cm}^2$  area. Similar measurements for  $J_{SC}$  are shown in Figure 9 demonstrating relative gains of  $\sim 0.36\%$  and  $0.96\%$  for  $130$  and  $64\text{-cm}^2$  areas. Planar cells also show slightly enhanced efficiency response for smaller areas, although no short-circuit current gain is observed. The enhanced response from smaller regions can be attributed to the texture non-uniformity at the edges. In most of the RIE-texturing work described here, the cell periphery of  $\sim 1\text{-}3\text{-cm}$  width remain almost planar. In addition, there is a transition region spanning few millimeters wide in which the texture becomes planar. Both of these features negatively impact cell performance, thus, leading to improved performance from smaller areas in which almost 100

% of the surface area is textured. By extending texture to the edges, this area-related performance anomaly should be eliminated.

#### 4. SOLAR CELLS PROCESSED AT SIEMENS

As part of a collaborative effort between SNL and Siemens/Shell, 100-cm<sup>2</sup> area tricrystalline wafers were conditioned textured w/nitric DRE at GI and processed into solar cells at Siemens. The emitter formation techniques at Siemens are based on tube furnace diffusion, although similar TiO<sub>2</sub> anti-reflection films are used. Solar cells were characterized as a function of texture process with TiO<sub>2</sub> ARC; RCA clean was used on all solar cells. Figure 10 shows averaged cell efficiency for two texture processes used, namely conditioned and Ti-assisted. For the processing at Siemens, cells without RCA treatment have not been evaluated. Efficiency measurements in Figure 10 show that conditioned texture process is superior to the Ti-assisted texture process, and both texture processes are superior to planar controls. The efficiency of the conditioned RIE-textured surface subjected has been improved by ~ 5.6 % relative to the planar controls. Similar results for the short circuit current are shown in Figure 11 demonstrating ~ 4.5 % improvement in conditioned textured process relative to the planar controls. These performance gains are relatively modest, substantial future gains may be realized by using an alkaline-based DRE and extending texture uniformity to the wafer edges.

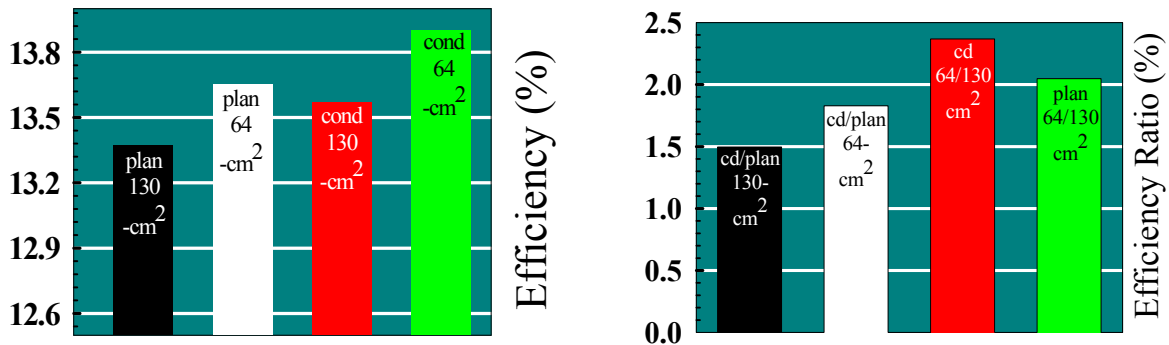


Figure 8. ANU Solar cell efficiency (left) and efficiency ratios relative to the planar controls (right) for the 130-cm<sup>2</sup> and 64-cm<sup>2</sup> cell areas, measurements are from the same cells before and after dicing.

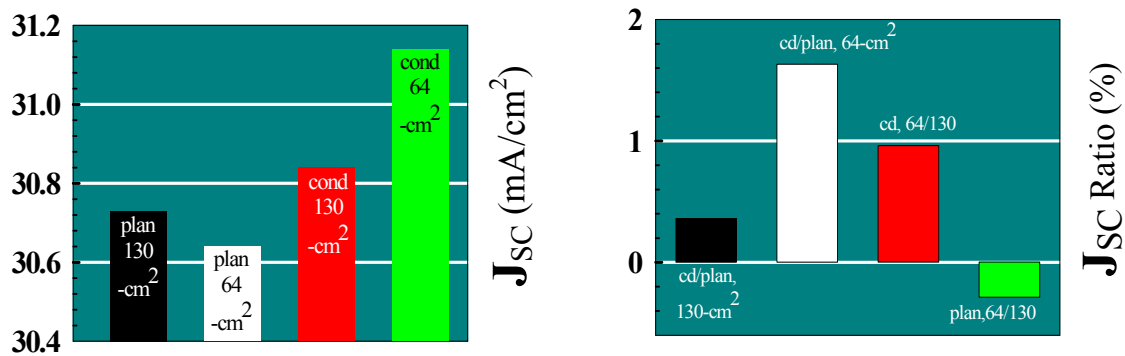


Figure 9. ANU Solar cell J<sub>SC</sub> (left) and J<sub>SC</sub> ratios relative to the planar controls (right) for the 130-cm<sup>2</sup> and 64-cm<sup>2</sup> areas, measurements are from the same cells before and after dicing.

## 5. SOLAR CELLS PROCESSED AT SANDIA NATIONAL LABORATORIES

Several texture processes were investigated at Sandia National Laboratories to determine surface profiles beneficial for solar cell performance. All the solar cells fabricated at SNL had an area of 42-cm<sup>2</sup>, the mc-Si material was provided by BP Solar.

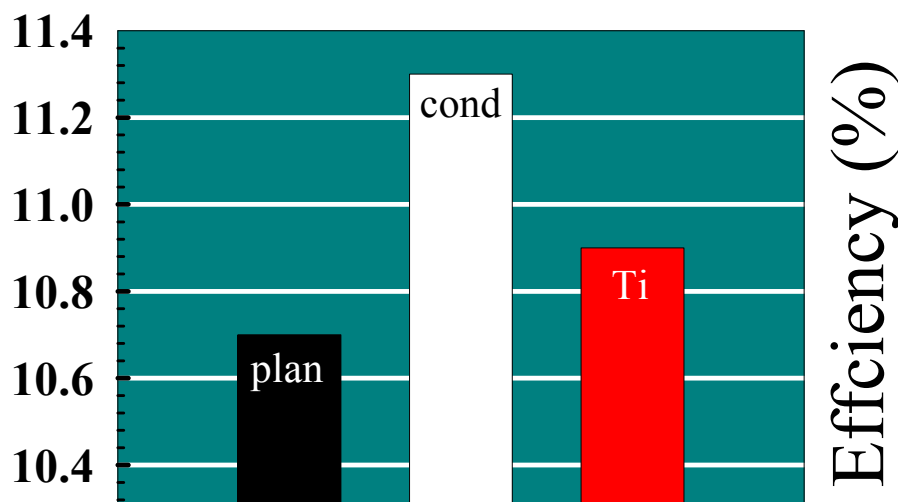


Figure 10. Siemens Solar cell efficiency measurements for both planar and RIE-textured cells with DRE using either Conditioned or Ti-assisted RIE processes; all subjected to RCA clean.

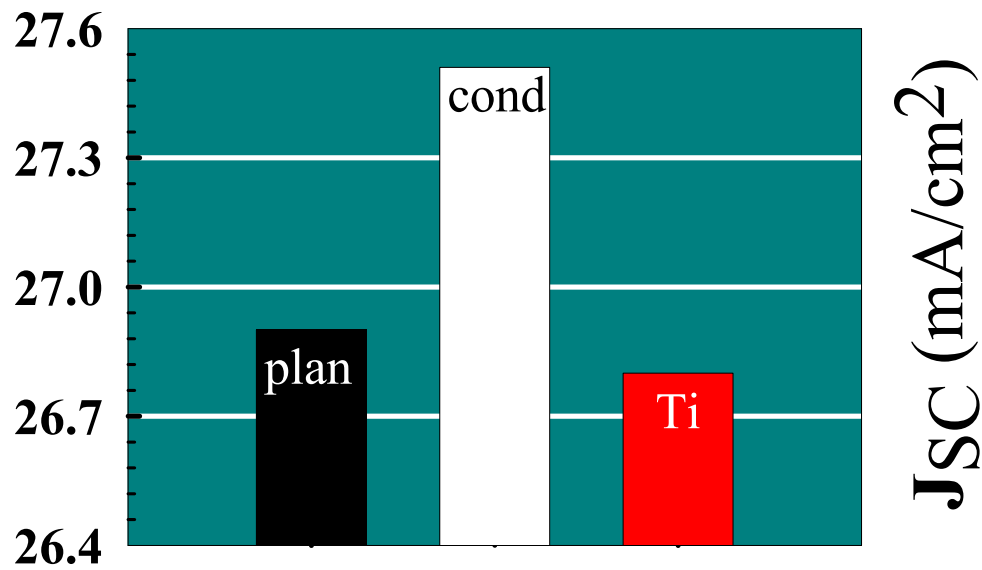


Figure 11. Siemens Solar cell  $J_{SC}$  measurements for both planar and RIE-textured cells with DRE using either Conditioned or Ti-assisted RIE processes; all cells were subjected to RCA clean.

The emitter formation process was a tube furnace diffusion using  $POCl_3$ , and a PECVD nitride ARC was used. All RIE-textured surfaces were subjected to RCA clean followed by nitric acid based DRE treatment prior to solar cell processing. Figure 12 shows efficiency performance for three texture profiles shown in Figure 1. We notice that except for the Cr-assisted texture, the two other textured surfaces significantly outperform planar controls with overall gains of  $\sim 6.62\%$  and  $\sim 5\%$  for conditioned and Al-assisted textures respectively. Figure 13 shows similar measurements for the short circuit current demonstrating gains of  $\sim 3.44\%$ ,  $7.19\%$  and  $4.28\%$  for Cr, conditioned, and Al-assisted texture processes respectively.

Although overall efficiencies of SNL solar cells are not as high as the ANU cells, the texture performance trend is similar to Siemens results except for significantly superior performance of the SNL textured cells. Further improvements in overall efficiency and textured cell performance are expected by employing an alkaline-based damage removal etch treatment.

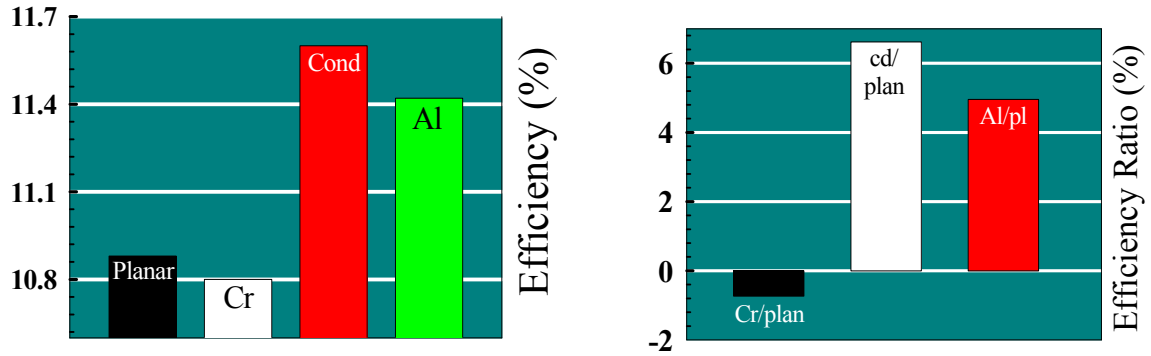


Figure 12. Sandia Solar cell efficiency (left) and efficiency ratios relative to the planar controls (right) for the three texture profiles shown in Figure 1, for comparison, planar cell efficiencies are also plotted.

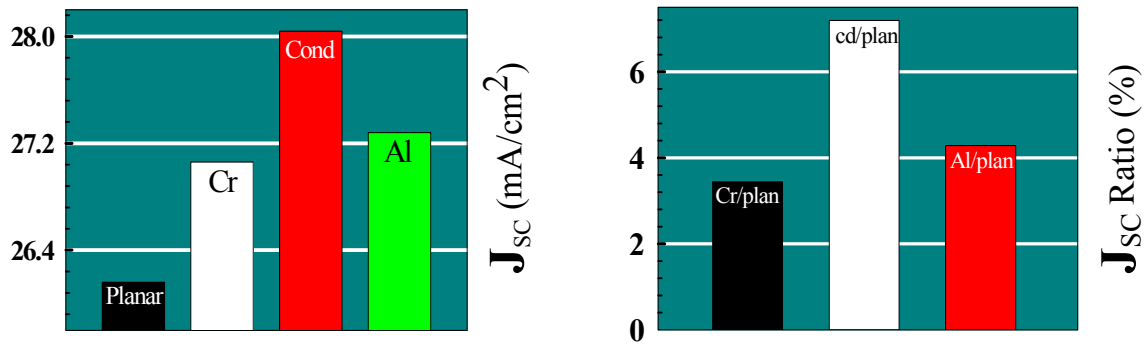


Figure 13. Sandia Solar cell  $J_{sc}$  (left) and  $J_{sc}$  ratios relative to the planar controls (right) for the three texture profiles shown in Figure 1, for comparison, planar cell efficiencies are also plotted.

## 6. SOLAR CELLS PROCESSED AT GEORGIA INSTITUTE OF TECHNOLOGY

In collaboration with Georgia Institute of Technology (Ga Tech), a number of small area ( $\sim 4$  cm<sup>2</sup>) RIE-textured solar cells were evaluated. The mc-Si material was provided by BP Solar, GI did texturing work, RCA cleaned, RIE-textured cells with and without nitric-based DREs were evaluated. All solar cells were coated with PECVD nitride anti-reflection films. All the data shown here was averaged from nine 4-cm<sup>2</sup> area cells fabricated on a 4" diameter BP Solar mc-Si wafer. Figure 14 shows averaged efficiency measurements for cells without and with DRE treatments. We notice that even without DRE treatment, conditioned texture process is slightly superior to the controls. This is in contrast to most of the work described earlier, and is probably due to improved surface passivation techniques. Incorporation of nitric DREs significantly

improves the performance of all textured cells with a maximum efficiency of  $\sim 14.2\%$  for the conditioned texture process. Figure 15 shows similar response for short circuit current from textured surfaces without the DRE treatment. Figure 16 shows that a maximum gain of  $\sim 8\%$  in efficiency is achieved by conditioned texture process combined with a nitric based DRE and RCA treatment. Finally, Figure 17 demonstrates a maximum gain of  $\sim 13\%$  for the conditioned texture. Based on recent work with alkaline based DRE treatments, we expect these gains to extend to  $\sim 20\%$  absolute improvements relative to controls.

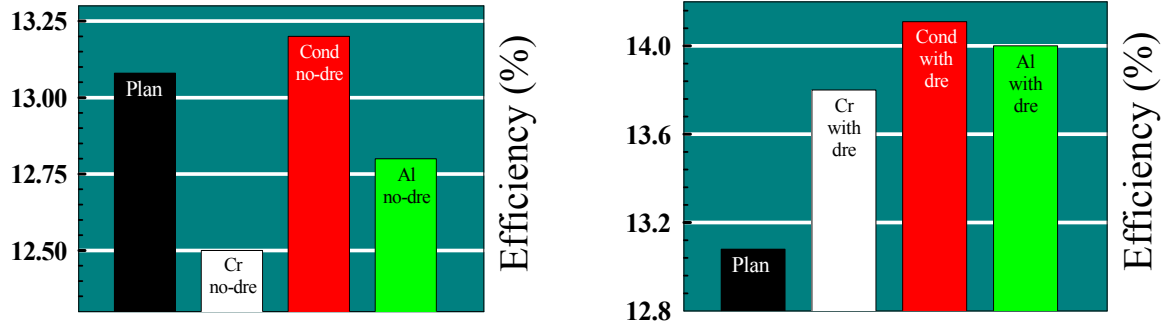


Figure 14. Ga Tech Solar cell efficiency without DRE (left) and with nitric DRE (right) for the three texture profiles shown in Figure 1, for comparison, planar cell efficiencies are also plotted.

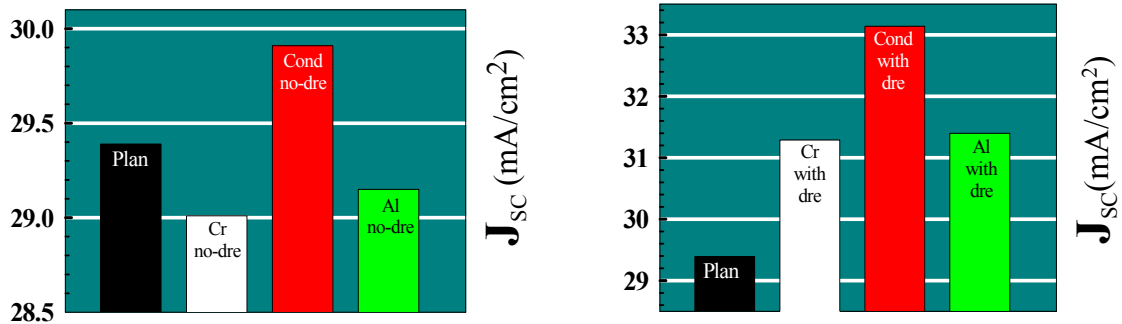


Figure 15. Ga Tech Solar cell  $J_{sc}$  without DRE (left) and with nitric DRE (right) for the three texture profiles shown in Figure 1, for comparison, planar cell efficiencies are also plotted.

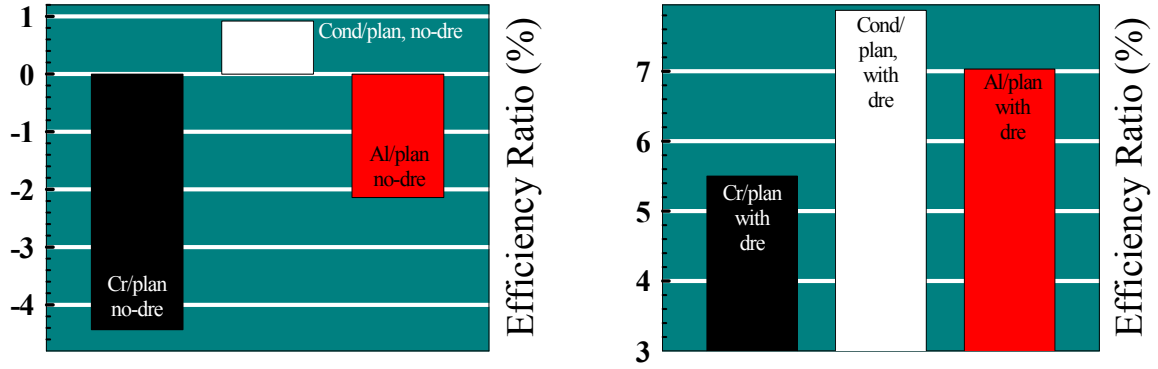


Figure 16. Ga Tech Solar cell efficiency gain ratios to controls without DRE (left) and with nitric DRE (right) for the three texture profiles shown in Figure 1.

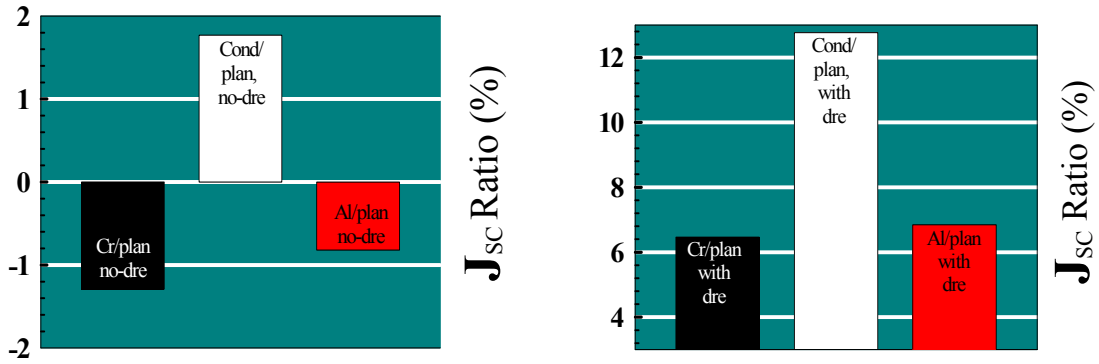


Figure 17. Ga Tech Solar cell  $J_{sc}$  gain ratios relative to controls without DRE (left) and with nitric DRE (right) for the three texture profiles shown in Figure 1.

## 7. SUMMARY AND FUTURE WORK

The random reactive ion etching texturing techniques have been adapted to several mc-Si solar cells resulting in significant performance gains. Use of inexpensive, wet-chemical damage removal treatments has eliminated RIE-induced surface damage and contamination. Table 1 summarizes some of the performance gains achieved. We notice that RIE-textured solar cell gains increase substantially as cell areas are reduced, except for the Siemens cells. The texture performance correlation with cell area can be attributed to several factors listed below.

- a) In most cases, RIE-textures do not extend to wafer edges leaving almost as much as 20 % of the area relatively planar.
- b) There is also a transition region from texture to planar at the sample edges. The profiles in this transition region are not beneficial to the solar cell performance.
- c) The alkaline-based DRE treatment has not yet been optimized, an optimized DRE process will lead to significant performance boost.
- d) Most PV manufacturers use  $\text{TiO}_2$  anti-reflection films, these may not be suitable for the RIE-textured solar cells. The highest efficiencies on both large ( $130 \text{ cm}^2$ , ANU processing) and small ( $4 \text{ cm}^2$ , Ga Tech processing) area solar cells have been achieved with nitride AR films that provide surface passivation.
- e) The emitter formation techniques employed so far have been developed for large textures and planar surfaces. The nano and micro-scale feature dimensions typical of RIE-texturing process may require modification of the emitter formation process that provides better surface passivation.

Table 1. RIE-Textured Solar Cells Relative to Controls

Cell Area ( $\text{cm}^2$ )	Processed At	Relative Efficiency Gain (%) (textured/planar)	Relative $J_{\text{SC}}$ Gain (%) (textured/planar)
130	BP Solar	0.88	1.03
130	ANU	1.5	0.36
100	Siemens	5.6	2.2
64	ANU	1.83	1.63
42	Sandia	6.62	7.19
4	Ga Tech	7.87	12.76

By addressing these issues in close collaboration with PV manufacturers, we believe that performance gains in  $\sim 10\text{-}20\%$  range may be realizable.



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